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**No. 27.—The Rate of Reaction in Solutions
containing Potassium Iodide, Potassium
Chlorate, and Hydrochloric Acid.**

BY
W. C. BRAY.

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**THE RATE OF REACTION IN SOLUTIONS
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POTASSIUM CHLORATE, AND
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By W. C. BRAY

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THE RATE OF REACTION IN SOLUTIONS CONTAINING POTASSIUM IODIDE, POTASSIUM CHLORATE, AND HYDROCHLORIC ACID

BY W. C. BRAY

The rate of the reaction between potassium chlorate, potassium iodide, and hydrochloric acid in aqueous solution has already formed the subject of more than one research; but, yet, no simple relation has been found between the concentrations of the reagents and the rate at which iodine is liberated from the solution.

The earliest data are contained in five tables at the end of an article by O. Burchard,¹ "*On the Oxidation of Hydrogen Iodide by the Oxyacids of the Halogens.*" His measurements are few in number; and, in the author's own opinion, "in spite of the precautions taken" (to exclude air) "the influence of the spontaneous decomposition of the hydrogen iodide is evident in all the experiments."

The next paper dealing with the subject, is W. H. Pennington and M. Seward's "*Investigation of a Case of Gradual Chemical Change.*"² The method employed — Harcourt and Esson's "Compensation Method" — is, however, quite unsuitable to the reaction studied,³ and the results of their measurements are widely different from those obtained by direct analysis.

The most recent contribution to the literature of this subject, "*The Chemical Kinetics of Oxidation,*"⁴ by H. Schlunegger and R. B. Warder, contains a large number of careful experiments; unfortunately, the plan of the work is of such a nature that, failing the existence of simple relations of a preconceived form, the results of the investigation do not lend themselves

¹ Zeit. phys. Chem. 2, 823 (1888).

² Proc. Roy. Soc. 45, 396 (1889).

³ J. M. Bell. Jour. Phys. Chem. 7, 61 (1903).

⁴ Am. Chem. Jour. 17, 754 (1895); 18, 23 (1896).

readily to the discovery of the relations actually existing. In reviewing their work, the authors come to the conclusion that a "satisfactory application of the law of mass has not yet been made to this reaction".¹ This paper is again referred to on page 114.

Plan of the experiments

The object of my own work has been to trace the effect on the rate produced by *changing the concentration of each one of the reagents individually*. With this end in view two methods² of experimenting were employed.

First Method.—In making up the solutions in which the rates of reaction were to be determined, one of the reagents was added in much less quantity than the others; the percentage change in the concentration of the latter (caused by chemical change in the solution) was thus rendered almost negligibly small, and the diminution in rate as the reaction progressed was due altogether to decrease in the concentration of the reagent present in small quantity.³ The effect on the rate caused by changes in the concentration of this substance was therefore easily ascertained. The relation between the rate and the concentrations of the other reagents was determined by comparing the results of a number of experiments in which the concentrations of the substances present in excess were varied. This is the plan pursued by Harcourt and Esson in their classical researches;⁴ it differs from Ostwald's "Isolation Method"⁵ by providing a means of determining the "order of the reaction" with respect to every reagent, without imposing the condition that each in turn must be present in (relatively) small quantity.

The *Second Method*, which may be called "the method of Constant Rates," is based upon the fact that, while the rate is dependent only on the concentrations, the total amount of

¹ Am. Chem. Jour. 18, 27 (1896).

² For the effect of the products of the reaction, see Series C, page 101.

³ Jour. Chem. Soc. 20, 460 (1867).

⁴ Ostwald, Lehrbuch, 2 Ed. II, 2, 238 (1897).

change in any interval depends upon the scale on which the experiment is carried out. It is thus often possible so to arrange matters, that while the amount of change accomplished in a suitable interval is sufficient for the requirements of an accurate analysis, yet the fractional alteration in the concentrations of the reagents involved is so small that the rate may be treated as practically constant during the interval. The amount of change divided by the time then gives the rate $dx/d\theta$ directly. This method is singularly applicable in the case of a reaction where the rate passes through a maximum or minimum, or where for any other reason the rate does not vary greatly with changes in the concentration; and in general whenever the substance produced can be determined accurately in the presence of relatively large quantities of the substances from which it is formed. As the concentrations of the products of the reaction are small in comparison with those of the reagents, complications may often be avoided by the use of the method of constant rates.

The effect of varying the concentration was studied through as wide an interval as possible, the limits being:—potassium chlorate $F/240^1$ to $3.3F$, potassium iodide, $F/40$ to $2F$, hydrochloric acid, $F/30$ to $2F$. As hydrochloric acid may be regarded as a mixture of chlorine-ion and hydrogen-ion, further experiments were necessary to determine the effect of the concentration of each of these individually.

The following series of experiments were carried out:—

Series A.—In connection with the method of analysis employed in Series B, a number of experiments on the acceleration of the reaction by iron salts.

Series B.—The concentration of the potassium chlorate much less than those of the other reagents. A method of determining chloric acid without the use of a pressure bottle is described.

Series C.—Experiments to determine the magnitude of the retardation caused by the iodine set free during the reaction.

¹ One gramme Formula weight in 240 liters.

Series D. — The concentration of the potassium iodide much less than those of the other reagents.

Series E. — The concentration of the acid much less than those of the other reagents.

Series F. — The chlorate and iodide present in comparable amounts, the acid in excess.

Series G. — The influence of the concentration of the chlorination on the rate. Experiments with sodium chloride.

Series H. — The influence of the concentration of the hydrogen-ion on the rate. Experiments with sulphuric acid.

Series J. — The influence of the concentration of the potassium iodide on the rate.

Method of operation

Evaporation of iodine. — Even comparative dilute solutions of iodine lose strength rapidly when exposed to the air at 30° C; for instance 200 cc of a $n/1000$ solution in a 300 cc beaker lost 5 percent of its iodine in ten minutes. The reacting mixture was consequently kept in small glass-stoppered bottles, and measurements were interrupted when the bottle was half empty. Even under these circumstances the last of a series of titrations is slightly affected by error due to loss of iodine.

Oxidation of hydriodic acid by air. — In order to avoid error from this source, all water used was boiled, cooled in a vacuum, kept under carbon dioxide, and delivered through a siphon. The pipettes, and the bottles in which the experiments were carried out were filled with carbon dioxide before using, and whenever the stopper was taken out of the bottle (to remove a portion for analysis) a slow current of carbon dioxide was passed in. The solutions used in making up the reacting mixtures were also freed from air, except in Series G and J, where the total duration of an experiment seldom exceeded ten minutes, and where the concentration of the potassium iodide was almost always small. In Series E, where the experiments extended over a period of several days, the reacting mixture was divided

among a number of small bottles, which were completely filled, and each of which held enough for two titrations only.

In a blank experiment, where the concentrations of both acid and iodide were greater than in most of my measurements, the iodine set free after five hours (during which the bottle had been opened five times to remove portions for titration) was equivalent to one drop only (0.05 cc) of the volumetric solution of sodium thiosulphate; when one unit of potassium chlorate was added to the same mixture, 24 cc of the thiosulphate solution were needed to neutralize the iodine liberated. Thus, even under unfavorable conditions, the error due to oxidation by the air, may be set at less than one-half of one percent.

*Details of a set of measurements.*¹—All solutions were brought to the temperature 30° C. A stoppered bottle (120 cc) was placed on a shelf in the thermostat and filled with carbon dioxide. Thirty-five cc of water, and 50 cc of 2F hydrochloric acid were pipetted in, then 5 cc F/3 potassium chlorate, and immediately afterwards 10 cc F potassium iodide. The stopper was inserted and the bottle shaken. As soon as possible (within a minute) 10 cc were pipetted into 100 cc of cold distilled water, and the iodine determined by sodium thiosulphate. Other titrations were made at known intervals. The time at which the first portion was removed was taken as $\theta = 0$ in the calculations, and the thiosulphate reading (0.1 or 0.2 cc) was subtracted from all subsequent readings; the readings thus corrected and expressed in cc F/100 thiosulphate, are recorded in the table under "100x."

Temperature.—All experiments were carried out at 30° C in a thermostat whose temperature did not vary more than 1/10 degree.

Chemicals and solutions employed.—The stock solutions of hydrochloric acid were standardized gravimetrically (silver chloride). The sodium chloride was prepared from the commercial salt by precipitation with hydrochloric acid and ignition. The titre of the volumetric solution of iodine was redetermined

¹ Expt. 27.

at intervals by comparison with weighed quantities of iodine sublimed with potassium iodide, or by titration against a solution of sodium arsenite; and the ratio between thiosulphate and iodine was determined before each set of analyses. The potassium chlorate was obtained from the commercial salt by recrystallizing and drying in a vacuum over sulphuric acid. The potassium iodide employed in Series A to E was weighed out for each experiment, and was free from alkali. For the other series two stock solutions were made up, 5 cc of which gave 1.1345 and 2.2650 grams AgI respectively, corresponding to 0.965 F and 1.938 F. These solutions contain free alkali, 10 cc requiring for neutralization 1.4 cc and 2.8 cc F/10 HCl respectively.

Measuring instruments.—The pipettes and burettes were calibrated for delivery, and only those which agreed within 0.1 percent among themselves were employed.

Explanation of the tables

At the head of each table is given the initial composition of the reacting mixture. The number following the letter A, multiplied by 2.0416, gives the weight in grammes of potassium chlorate per liter of the reacting mixtures; the number following B, multiplied by 16.6, gives the weight of potassium iodide; that after C, multiplied by 3.64, the weight of hydrogen chloride; that after D, multiplied by 3.545, the weight of chlorine added as hydrochloric acid and sodium chloride; and that after FeSO₄, multiplied by 15.2, the weight of ferrous sulphate—all in grammes per liter. For example, A = 1, B = 10, C = 10 signifies that the solution was F/60 (decinormal) with regard to the chlorate, and F (normal) with respect to iodide and acid at the beginning of the experiment.

Under θ is entered the time in minutes from the first measurement, and under 100x the number of cc F/100 thio-

¹ In a few cases an alkalimetrically equivalent quantity of sulphuric acid was used. (Tables 35 and 36).

sulphate equivalent to the free iodine liberated in 10 cc of the reacting mixture during that period.

The numbers under "T(1)," "T(5)," etc., are obtained from Tables, 1, 5, etc., by interpolation, and give the number of minutes in which the amount of iodine entered under "100x" was liberated in the experiments of those tables.

$R = 100 \, dx/d\theta$ is the initial rate, *i. e.*, the number of cc $n/100$ iodine liberated per minute in 10 cc of a reacting mixture of the composition given at the head of the table. It is obtained by multiplying the concentration of the substance present in small quantity by k_1 . Finally, k_1 is the "constant of the first order"; if the potassium chlorate be present in small quantity, $k_1 = 1/\theta \log \text{nat } A/(A-x)$.

Results of the Experiments

Series A. Acceleration by iron

In Expts. 1 and 2 the initial concentrations of the chlorate, iodide, and acid were the same, but in Ex. 2 a little ferrous sulphate (equivalent to $2\frac{1}{2}$ percent of the chlorate) was added. This slight addition multiplied the rate by 13.

In the case of Expts. 3 and 4 the acceleration is still more marked.

EXPTS. 1 AND 2.

A 1.0; B 8.75; C 8.85; FeSO₄ Ex. (1) none, Ex. (2) 0.025.

1.	100 x.	$k_1 \times 10^4$	k_1 corr.	2. θ	100 x	T(1)	T/ θ
42	3.2	7.80	6.97	10	8.6	120	12
122	9.3	8.00	—	34	28.1	445	13
188	13.4	7.66	7.28	75	49.4	950	13
194	13.9	7.73	—	108	65.08	1580	14
287	19.9	7.73	—	141	71.3	1840	13
335	22.5	7.61	7.25	172	77.5	—	—
454	28.9	7.52	7.25	204	72.6	—	—
655	38.5	7.41	—	—	—	—	—
733	41.5	7.30	7.25	—	—	—	—
1484	63.6	6.79	—	—	—	—	—
1493	63.9	6.84	—	—	—	—	—
1863	72.3	6.70	7.34	—	—	—	—

EXPTS. 3 AND 4.

A 0.25; B 2.44; C 2.46; FeSO₄ Ex. (3) none, Ex. (4) 0.05.

3. One reading only; θ , 4410; 100x, 4.0							
θ	21	(55)*	62	1395	1588	2881	3126
400 x	5.2	(16)	55.6	91.3	92.9	93.7	95.1

Series B. Potassium chlorate in small quantity

Effect of the Chlorate. — The (approximate) constancy of k_1 (Expt. 1) shows that the rate is proportional to the concentration of the potassium chlorate in the reacting mixture. This conclusion is supported by the constancy of k_1 in the experiments of this section, by the identity of k_1 in Expts. 5 and 6 (where the initial concentrations of the chlorate were different), and by the experiments of Series D, where the chlorate was doubled in excess. The only exception is referred to in Series E. The slight but regular decrease in k_1 as the reaction proceeds, is due to the slight decrease in the concentrations of the reagents present in excess. In the case of Expt. 1, I have applied the correction due to this cause, assuming that the rate is proportional to the first power of the concentration of the potassium iodide, and to the cube of that of the acid (see page 100). The constancy of " k_1 corr." leaves nothing to be desired.

EXPTS. 5 AND 6.

5. A 1.00; B 8.77; C 8.85.			6. A 0.5; B 8.77; C 8.85.		
θ	100 x	$k_1 \times 10^4$	θ	100 x	$k_1 \times 10^4$
15	1.4	9.2	30	1.35	9.2
72	6.7	9.5	83	3.5	8.7
106	9.4	9.3	162	6.7	8.7
139	11.05	8.5	241	9.45	8.5
213	15.2	7.8	332	13.1	8.3
262	19.8	8.2	593	21.5	9.2
1317	64.9	8.0	1413	39.4	10.8*
1462	67.15	7.8	1691	42.3	11.0*

R = 0.092

R = 0.046

* Interpolated.

Experiments 1, 2, 3, and 4 were carried out with stock solutions whose composition is not known with accuracy; they cannot be compared directly with the other experiments of this paper.

EXPT. 7.

7. A 1.0; B 17.5; C 8.85.

θ	$100x$	$k_1 \times 10^4$	T (5)	T/ θ
20	3.4	17.5	37	1.9
53	8.5	16.6	95	1.8
117	17.8	16.8	213	1.8
201	28.1	16.3	387	1.9
291	36.9	15.6	555	1.9
549	37.1	15.4	1050	1.9
1346	39.7	17.0	—	—
1609	44.6	17.7*	—	—

$$R = 0.175$$

Effect of the Iodide.—From a comparison of Expt. 6 with Expt. 7 and of Expt. 8 with Expt. 9, it follows that doubling the concentration of the potassium iodide multiplies the rate by about 1.8.

EXPTS. 8 AND 9.

8. A 0.98; B 9.8; C 9.9.

9. A 1.0; B 5.0; C 10.0.

θ	$100x$	$k_1 \times 10^4$	θ	$100x$	$k_1 \times 10^4$	T (8)	T/ θ
20	2.0	9.9	27	1.57	5.8	16	1.7
97	8.9	9.7	65	3.7	5.7	38	1.7
142	12.7	9.5	130	7.1	5.6	75	1.7
194	16.8	9.4	373	18.5	5.5	216	1.7
256	21.7	9.4	385	19.2	5.3	225	1.7
1347	74.0	9.9	1456	53.0	5.1	800	1.8
—	—	—	1640	57.2	5.3	899	1.8
—	—	—	2935	77.5	4.9	—	—

$$R = 0.99$$

$$R = 0.058$$

Effect of the Acid.—Increasing the amount of the acid present from 4.42 units to 8.85 multiplies the rate by 4.5 or 5.0 (Expts. 10 and 5). A further increase from 8.85 to 17.7 multiplies the rate by 7.7 or 8 (Expt. 11) so that the rate is proportional to

* The temperature of the thermostat rose during the night. (Expts. 6 and 7.)

the second or to the third power of the concentration of the acid depending on circumstances.

EXPTS. 10 AND 11.

10. A 1.0; B 8.77; C 4.42.					11. A 1.0; B 8.77; C 17.7.				
θ	100 x	$k_1 \times 10^4$	T (s)	θ/T	θ	100 x	$k_1 \times 10^4$	T (s)	T/ θ
40	0.83	2.0	9	4.4	34	19.6	64	263	7.7
99	1.90	1.9	21	4.7	60	32.4	65	472	7.8
323	5.4	1.7	60	5.4	93	47.14	68	791	8.5
481	8.4	1.8	95	5.1	172	66.3	63	1390	8.1
631	10.5	1.7	120	5.2	295	81.4	57	—	—
—	—	—	—	—	461	95.8	—	—	—

$$R = 0.020$$

$$R = 0.64$$

Series C. Influence of iodine on the rate

The difficulty experienced in finding a simple formula to describe the progress of reactions involving the oxidation of iodides, has been generally ascribed to the effect exerted upon the rate by the iodine liberated during the reaction.

Ostwald¹ showed by direct experiment that the reaction between bromic and hydriodic acids was retarded by the addition of iodine; Meyerhoffer² set up a formula to express the retardation as a function of the amount of iodine liberated, which was found to be inconsistent with the subsequent experiments of Burchard.³ Finally, Judson and Walker⁴ expressed the opinion that "the action of hydriodic acid on the oxygen acids of the halogens is of too intricate a nature to give any satisfactory numerical results."

Comparing Expt. 12 with Expt. 5, it will be seen that the retardation brought about by saturating the reacting mixture with iodine (8.7 units) is at the outside 15 to 20 percent; the effect of the iodine liberated in Expt. 5 (0.7 unit after 1500 minutes) may therefore safely be neglected. As in Expt. 12, the amount of

¹ Zeit. phys. Chem. 2, 127 (1888).

² Ibid. 2, 585 (1888).

³ Ibid. 2, 796 (1888).

⁴ Jour. Chem. Soc. 73, 410 (1898).

iodine dissolved was sufficient to convert one-half of the iodion into triiodion, the retardation is considerably less than might have been anticipated.

EXPT. 12.

A 1.0; B 8.77; C 8.85; Iodine 8.7.

θ	$100x$	$k_1 \times 10^4$
29	1.7	5.7
50	5.6	9.6
83	5.6	6.9
152	12.5	8.7
203	12.7	6.7
285	20.6	8.0
360	25.0	7.8
1454	59.2	6.8
1577	63.7	6.4

Method of Analysis. — Every precaution was taken to exclude air from the solution. A little potassium iodide was added to dissolve precipitated iodine. The iodine was next reduced by 0.25*N* sodium sulphite, added slowly from a burette with constant shaking (blank experiments having shown that otherwise there was a loss of chlorate by reduction), starch serving as indicator. A drop or two of dilute solution of potassium permanganate were then added to restore the blue color; this was necessary in order to make sure that there was no excess of sulphite. The chloric acid in this mixture was then determined by reducing it with hydriodic acid, and titrating the iodine liberated.

The reduction may be effected by adding strong hydrochloric acid and heating the mixture in the special digesting bottle described by Mohr;¹ in the presence of a trace of iron ($\frac{1}{4}$ cc normal ferrous sulphate), however, the reaction takes place so quickly at 30° C that the determinations were made in ordinary stoppered bottles standing in the thermostat in which the rates of reaction were being measured.

¹ Mohr's "Titrimethode," 7 ed., page 364. The use of the digesting bottle could probably be avoided in other cases by the same means.

Blank experiments showed that the results of chlorate determinations carried out as described are independent of the amount of iron salt added, and that they are in agreement with those obtained by help of the digesting bottle, or by the use of ferrous sulphate and potassium permanganate.¹ The ferrous sulphate added is probably oxidized, in part, at all events, by the chloric acid; but if so, it is again reduced by the large excess of hydriodic acid present in the solution.

Series D. Potassium iodide in small quantity

Effect of the Iodide. — If the rate were proportional to the concentration of the potassium iodide, the rate of Expt. 13 (A 9.8; B 1.0; C 10.23) would be almost the same as that of Expt. 5 (A 1.0; B 8.77; C 8.8). In reality the former is much greater. Moreover, k_1 in Expt. 13 is in no sense a constant, in fact the average rate of the reaction, as measured by the quotient x/θ , only changes 20 percent, while the concentration of the iodide falls from 1.0 to 0.05 unit. Another peculiarity is revealed by Expts. 18, 19, and 20, viz; that either increasing or decreasing the initial concentration of the iodide over that in Expt. 13 accelerates the reaction.

EXPT. 13.
A 9.80; B 1.0; C 10.23.

θ	100 x	100 x/θ	$\dots \times 10^4$
24	5.9	0.245 (R)	25
81	19.6	0.242	26
123	28.5	0.232	27
194	42.8	0.221	28
201	42.8	0.213	28
264	56.9*	0.214	32
305	65.4*	0.211	35
337	72.0*	0.211	37
479	94.7*	0.200	44

* The rate decreases until iodine is precipitated from the reacting mixture and then remains much more constant. In the last four measurements iodine separated out. The reacting mixture was sealed in glass tubes, 10 cc in each, and after the proper interval the top of the tube was broken and the contents poured into 100 cc of cold water. The iodine was dissolved with a little potassium iodide, and added to the rest, and the titration proceeded with in the usual manner.

¹ Mohr. 1. c. page 270.

Effect of the Chlorate. — Expts. 13, 14, and 15 show that the rate is proportional to the concentration of the potassium chlorate.

Effect of the Acid. — Expts. 13, 16, and 17 show that doubling the concentration of the acid multiplies the rate by 6 or by 7 respectively.

EXPTS. 14 AND 15.

14. A 19.60; B 1.0; C 10.23.					15. A 4.90; B 1.0; C 10.23.				
θ	$100x$	$100x/\theta$	T (13)	T/ θ	θ	$100x$	$100x/\theta$	T (13)	θ/T
21.5	8.4	0.390 (R)	36	1.7	33	3.8	0.115 (R)	15.5	2.1
58	22.4	0.384	95	1.7	70	8.0	0.114	33.0	2.1
88	32.8	0.370	142	1.7	161	17.7	0.109	74	2.2
115	41.96	0.356	187	1.7	182	18.7	0.103	78	2.3
—	—	—	—	—	207	22.2	0.107	92	2.2
—	—	—	—	—	311	31.5	0.100	137	2.2
—	—	—	—	—	359	35.7	0.100	155	2.3

EXPTS. 16 AND 17.

16. A 9.80; B 1.0; C 20.46.					17. A 9.80; B 1.0; C 5.11.				
θ	$100x$	$100x/\theta$	T (13)	T/ θ	θ	$100x$	$100x/\theta$	T (13)	θ/T
5	8.72	1.74 (R)	35.5	7.1	28	1.51	0.054	6.2	4.5
17	27.6	1.60	119	7.0	142	5.6	0.040 (R)	23	6.1
20	31.6	1.58	136	6.8	201	2.0	0.040	32	6.3
26	40.46	1.55	183	7.0	267	11.1	0.041	45	5.9
—	—	—	—	—	361	15.3	0.042	63	5.7
—	—	—	—	—	1332	45.5	0.034	215	6.2

EXPTS. 18, 19 AND 20.

18. A 9.80; B 0.5; C 10.23. 19. A 10.0; B 1.93; C 10.0. 20. A 10.0; B 2.9; C 9.81.

θ	$100x$	$100x/\theta$	θ	$100x$	$100x/\theta$	θ	$100x$	$100x/\theta$
19	5.3	0.279 (R)	21	6.2	0.296 (R)	24	9.5	0.395 (R)
39	11.3	0.290	72	19.9	0.270	70	24.4	0.350
59	17.1	0.289	164	41.0	0.250	120	41.2	0.343
74	20.7	0.280	241	53.5	0.222	196	62.6	0.320
—	—	—	338	71.3	0.211	275	81.3	0.296
—	—	—	408	81.3	0.197	360	100.4	0.274
—	—	—	—	—	—	460	116.4	0.253

Series E. Hydrochloric acid in small quantity

Owing to the alkalinity of the potassium iodide, the concentrations of the acid in the experiments of this series are not simple multiples.

Effect of the Acid. — The rate is proportional to the concentration of the acid when 0.37 to 1.81 units are employed (Expts. 22, 21, 23).

Effect of the Chlorate. — Doubling the concentration of the potassium chlorate only slightly increases the rate (Expts. 21 and 26).

Effect of the Iodide. — Increasing the concentration of the potassium iodide from 10 to 18 units adds 20 percent to the rate (Expts. 21 and 25).

EXPTS. 21, 22 AND 23.

21. A 10; B 10; C 0.88.			22. A 10; B 10; C 0.37.			23. A 10; B 10; C 1.81.		
θ	$100x$	$k_1 \times 10^4$	θ	$100x$	$k_1 \times 10^4$	θ	$100x$	$k_1 \times 10^4$
1206	12.4	1.24	1320	5.7	1.29	83	2.1	1.40
1525	16.7	1.40	1413	6.7	1.40	1163	26.8	1.38
1555	16.9	1.36	2546	10.9	1.36	2562	53.1	1.33
2592	26.0	1.34	5336	14.5	1.04	5432	80.2	1.27
5452	46.8	1.38	5725	14.6	0.90	5832	94.5	1.27
5848	49.0	1.38	9691	15.0	0.53	7209	105.9	1.24
9905	66.1	1.40	1795	15.1	—	—	—	—
12672	66.6	1.10	—	—	—	—	—	—
19896	79.6	1.17	—	—	—	—	—	—
R = 0.0109			R = 0.0047			R = 0.0253		

EXPTS. 24, 25 AND 26.

24. A 10; B 10; C 3.85.			25. A 10; B 18; C 0.77.			26. A 20; B 10; C 0.88.		
θ	$100x$	$k_1 \times 10^4$	θ	$100x$	$k_1 \times 10^4$	θ	$100x$	$k_1 \times 10^4$
60	6.9	3.11	22	0.3	1.77	303	4.1	1.34
312	33.4	2.9	1040	10.3	1.38	1320	16.3	1.54
1383	107.0	2.34	4120	32.2	1.31	1730	20.1	1.49
2896	160	1.86	14246	39.2	—	—	—	—
3396	203	2.14	—	—	—	—	—	—
R = 0.119			R = 0.013			R = 0.012		

Series F. Potassium chlorate and potassium iodide in comparable quantities; hydrochloric acid in excess

Effect of the Chlorate and of the Iodide.—Throughout each experiment of this series, k_2 is fairly constant.¹

Comparing the values of k_2 for the different experiments, it will be seen that doubling the initial concentration of the chlorate leaves k_2 unaltered (Expts. 27 and 29; 28 and 30), while doubling that of the iodide diminishes k_2 (Expts. 27 and 28; 29 and 30; 31 and 27). Hence the rate is proportional to the concentration of the chlorate, and less than proportional to that of the iodide.

Effect of the Acid.—Increase from 4.98 to 10.1 units (Expt. 33) multiplies the rate by 4 or 4.8; further increase from 10.1 to 15.2 multiplies it by 3.5 (Expt. 32).

EXPTS. 27, 28 AND 29.

27. A 1.0; B 0.965; C 10.10. 28. A 1.0; B 1.93; C 9.95. 29. A 2.0; B 0.965; C 10.1.

θ	100 x	$k_2 \times 10^4$	θ	100 x	$k_2 \times 10^4$	θ	100 x	$k_2 \times 10^4$
150	3.3	2.29	1072	24.6	1.49	90	3.8	2.16
1085	18.5	2.09	1195	26.7	1.40	171	6.9	2.13
1262	21.2	2.13	1396	29.3	1.36	1168	35.1	2.05
1390	23.0	2.18	2441	44.1	1.36	1269	36.5	2.00
2448	33.7	2.08	2541	45.0	1.35	—	—	—
—	—	—	5321	66.6	1.48	—	—	—
—	—	—	5730	69.7	1.33	—	—	—

R = 0.0229

R = 0.0298

R = 0.0432

EXPTS. 30 AND 31.

30. A 2.0; B 1.93; C 9.95.

31. A 1.0; B 0.482; C 10.16.

θ	100 x	$k_2 \times 10^4$	θ	100 x
126	7.5	1.56	129	2.4
213	12.9	1.42	279	5.05
360	18.5	1.42	385	6.7
1366	54.8	1.41	1362	18.5

R = 0.062

R = 0.0186

¹ $k_2 = 1/(A-x) - 1/A$.

EXPTS. 32 AND 33.

32. A 1.0; B 0.965; C 15.2.					33. A 1.0; B 0.965; C 4.98.				
θ	$100x$	$k_2 \times 10^4$	T (27)	T θ	θ	$100x$	$k_2 \times 10^4$	T (27)	θT
100	7.0	7.53	360	3.6	185	1.07	0.584	47	4.0
160	10.6	7.41	370	3.5	331	1.7	0.522	76	4.3
1181	48.5	7.98	—	—	1136	5.8	0.462	300	4.4
—	—	—	—	—	4275	15.7	0.436	880	4.8
—	—	—	—	—	14385	37.9	0.426	—	—
—	—	—	—	—	15766	42.1	0.462	—	—

$$R = 0.0753$$

$$R = 0.00589$$

Series G. Influence of the chlorine-ion on the rate

Assuming complete dissociation (or equal dissociation) of the potassium chlorate, potassium iodide, and hydrochloric acid, A, B, and C of the experiments of the preceding series represent the concentrations of the chlorate-ion, the iod-ion, and the hydrogen-ion respectively. If D stand for the concentration of the chlorine-ion, then in all the experiments so far, $C = D$. In Expt. 34, however, D is varied independently of C, by adding sodium chloride to the reacting mixture. The values of R are obtained by the "Method of Constant Rates." That the acceleration is proportional to the amount of salt added, is evidenced by the agreement between the observed values of R, and those calculated by the formula $R = 0.097 + 0.009n$.

An experiment with double the amount of potassium chlorate gave double the acceleration per unit of sodium chloride added.

Series H. Influence of the hydrogen-ion on the rate

The results of the preceding series in which the influence of the chlorine-ion on the rate was determined, render it possible to calculate the effect due to the hydrogen-ion from experiments in which the concentrations of both (i. e., of the hydrochloric acid) were varied.

From Ex. 13:—

$$A = 9.8, B = 1.0, C = D = 10.2 \dots \dots R = 0.245$$

by means of the formula of page 107 the value of R for the hypothetical experiment : —

$$A = 9.8, B = 1.0, C = 10.2, D = 5.1 \dots R = 0.153$$

may be calculated, thus : —

$$R = 0.245 - 2 \times 0.009 \times 5.1 = 0.153.$$

Comparing with Expt. 17 : —

$$A = 9.8, B = 1.0, C = D = 5.1 \dots R = 0.04$$

it appears that doubling the concentration of the hydrogen-ion multiplies the rate by 4.

EXPT. 34.

$$A \ 4.967; B \ 0.995; C \ 10.01; D \ 10.01 + n.$$

n	D	R	$R \text{ calc.}$
0	10.01	0.091	(0.091)
2	12.01	0.104	0.115
5	15.01	0.135	0.142
10	25.01	0.187	(0.187)
18	28.01	0.296	0.259*

EXPTS. 35 AND 36.

$$A \ 10.0; B \ 0.965; C \ (H_2SO_4) \text{ Expt. 35, } 10.1; \text{ Expt. 36, } 14.54.$$

35. θ	100 x	36. θ	100 x	T (35)	T/ θ
40	2.14	21	1.98	—	—
169	6.62	65	5.6	128	2.0
360	12.9	120	9.8	262	2.2
1327	35.7	185	14.4	400	2.2
1417	38.0	222	19.6	—	—

$$R = 0.054$$

$$R = 0.094$$

Similarly, comparing Expt. 13 with Expt. 16 : —

$$A = 9.8, B = 1.0, C = D = 20.46 \dots R = 1.74$$

addition of 10.23 units of chlorine to Expt. 13 would give : —

$$A = 9.8, B = 1.0, C = 10.41, D = 20.46 \dots R = 0.43$$

* In several other experiments I have observed that when large excess of sodium chloride is used the rate is greater than that calculated by the linear formula.

and as in the former case, doubling the concentration of the hydrogen-ion quadruples the rate.

Thus, within the limits 5 and 20 units of acid, the rate is proportional to the square of the concentration of the hydrogen ion.

By way of control, in two experiments (Expt. 35 and 36) the hydrochloric acid was replaced by sulphuric acid.¹ Increasing the acid from 10.1 to 14.54 units multiplied the rate by 2.0 or 2.2; thus the rate is proportional to the square of the concentration of the sulphuric acid $(14.54/10.1)^2 = 2.07$. The rate in Expt. 35 ($R = 0.054$) is somewhat less than that calculated from the experiments with hydrochloric acid (Expt. 13), *viz.* $0.245 \div 2 \times 0.009 \times 10.2 = 0.061$; a further correction of two percent, for the difference of one percent in the amount of acid in the two experiments, would bring the calculated value down to 0.060; the difference remaining may be ascribed, in part at least, to the difference between the electrolytic dissociation of the two acids.

When the amount of hydrochloric acid present is greater than 20 units, the observed rate is much greater than that calculated by the method just described, for instance:—

Expt. 37. $A = 10$; $B = 0.965$; $C = 30.45$; $R_{obs.} = 14$; $R_{calc.} = 5.23$.

On the other hand, when the reacting mixture contains little acid and much salt (Series E) the rate is slower.

Series J. Influence of the potassium iodide on the rate

Owing to the alkalinity of the stock solutions of KI, C varies throughout the tables. The effect on the rate has been allowed for in "*R corr.*" by assuming that R is proportional to C^2 .

The conclusion reached by comparing Expts. 13, 18, and 19 (page 103) is confirmed by Expts. 38, 39, and 40, which show that, as the concentration of the potassium iodide is increased, the rate falls off, passes through a minimum and rises again. After passing the minimum, the acceleration per unit of iodide added

¹ Standardized by comparison with the stock solution of hydrochloric acid.

increases slightly with increase in the concentration of the iodide in the reacting mixture; but, as a first approximation, the acceleration per unit may be regarded as constant when $B \geq 1$; "R calc." in Tables 38, 39, 40, has been obtained on this assumption. Doubling the concentration of the potassium chlorate somewhat more than doubles the acceleration; doubling that of the acid multiplies it by 6. Increase in the concentration of either chlorate or acid causes the minimum to move towards $B = 0$.

EXPT. 38.

A 4.967; B 0.995 n .

n	C	R	R corr.	R calc.
1 16	10.01	0.109	0.109	—
1 8	10.01	0.097	0.097	—
1 4	10.00	0.068	0.068	—
1 2	10.00	0.088	0.088	—
1	9.98	0.097	0.097	0.097
2	9.95	0.150	0.151	0.161
4	9.84	0.271	0.277	0.289
10	9.71	0.630	0.670	0.670

$$(R \text{ calc.} = 0.097 + 0.064 n - 1)$$

EXPT. 39.

A 9.935; B 0.995 n .

n	C	R	R corr.	R calc.
1 32	10.01	0.199	0.199	—
1 16	10.01	0.176	0.176	—
1 8	10.01	0.157	0.157	—
1 4	10.00	0.163	0.163	—
1 2	10.00	0.168	0.168	—
1	9.98	0.198	0.199	0.199
2	9.95	0.290	0.292	0.305
5	9.86	0.610	0.624	0.624

$$(R \text{ calc.} = 0.198 + 0.106 n - 1)$$

EXPT. 40.

A 4.967; B 0.995 *n*.

<i>n</i>	C	R	R corr.	R calc.
1/16	5.00	0.034	0.034	—
1/8	5.00	0.028	0.028	—
1/4	5.00	0.0203	0.0203	—
1/2	4.99	0.0179	0.0180	0.0179
1	4.98	0.0228	0.0230	0.0230
2	4.95	0.0315	0.0321	0.0333
5	4.86	0.0550	0.0581	0.0655
10	4.71	0.105	0.117	0.117

$$(R \text{ calc} = 0.023 + 0.0103 \, n - 1)$$

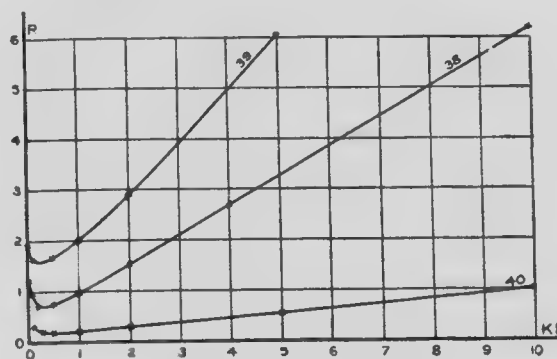


Fig. 1 Exps. 38, 39, and 40.

Summary of the results of the measurements

I. Volumetric determination of chlorates. If ferrous sulphate be added to the mixture of hydrochloric acid and potassium iodide in the iodometric determination of chlorate, the use of a digesting bottle may be dispensed with.

II. The rate at which iodine is liberated in solutions containing potassium chlorate, potassium iodide, and hydrochloric acid, is proportional to the concentration of the chlorate and to the square of the concentration of the hydrogen-ion (between $C = 5$ and $C = 20$); and is a linear function of the concentration of the chlorine-ion, and of that of the potassium iodide (when $B \geq 1$).

Expressed in the form of an equation this statement becomes

$$dx/d\theta = (A - x)(C - x)^2[k_a(B - 1 - x) + k_b(C + 1/6x)] \dots \text{Eq. I.}$$

In this equation no account is taken of the retardation of the reaction by iodine.

Numerical values for k_a and k_b may be obtained as follows: In Table 35 ($A = 5$, $C = 10$), $dx/d\theta = 0.01$, $R = 0.00097 + 0.00009(B - 1)$; that is, $\Delta R/\Delta B = 5 \times 10^2 \times k_b = 0.00009$; whence $k_b = 0.00000018$. Similarly from Table 38, $k_a = 0.00000128$.

Using these numbers, I have calculated values of R for all my experiments,¹ and compared them with the observed values (Table 41). The agreement is better than could have been expected, considering that in many of the experiments the conditions of concentration differ materially from those laid down in the second paragraph of this summary.

Molecular interpretation of the results

Assuming that the rate of a chemical reaction is proportional to the concentration of each reagent, raised to a power equal to the number of molecules entering into the reaction, the kinetic equation of the preceding section corresponds to the simultaneous occurrence of the two reactions



followed by instantaneous oxidation of hydriodic acid by the ClO_2H , ClOH , and IOH .

The reactions assumed are analogous to that adduced in the case of the oxidation of hydrogen bromide by bromic acid;² and the formation of IOH as the product of oxidation of an iodide is in accord with the results of Roebuck's research on the reaction between arsenic acid and potassium iodide.³

¹ Except Expts. 1-4; see note, page 99.

² Jour. Chem. Soc. 73, 420 (1898).

Jour. Phys. Chem. 6, 365 (1902).

TABLE XL1.

Ex.	A	B	C	R obs.	R calc.	Ex.	A	B	C	R obs.	R calc.
5	1.00	8.77	8.85	0.092	0.090	29	2.0	0.965	10.10	0.0432	0.036
6	0.5	8.77	8.85	0.046	0.045	30	2.0	1.93	9.95	0.062	0.059
7	1.00	17.5	8.85	0.175	0.178	31	1.0	0.482	10.16	0.0186	(B < 1)
8	0.98	9.8	9.9	0.099	0.125	32	1.0	0.965	15.2	0.0753	0.063
9	1.00	5.0	10.0	0.058	0.065	33	1.0	0.965	4.98	0.0059	0.0022
10	1.00	8.77	4.42	0.020	0.021	34	4.967	0.995	10.01	0.091	0.090
11	1.00	8.77	17.7	0.64	0.411	"	4.967	0.995	10.01	0.104	0.108
12	1.00	8.77	8.85	—	(iodine)	"	4.967	0.995	10.01	0.135	0.134
13	9.80	1.0	10.23	0.245	0.019	"	4.967	0.995	10.01	0.187	0.224
14	19.60	1.0	10.23	0.390	0.380	"	4.967	0.995	10.01	0.296	0.251
15	4.90	1.0	10.23	0.115	0.095	35	10.0	0.965	10.1	0.054	(H ₂ SO ₄)
16	9.80	1.0	20.46	1.74	1.51	36	10.0	0.965	14.54	0.094	(H ₂ SO ₄)
17	9.80	1.0	5.11	0.040	0.024	37	10.0	0.965	30.45	0.094	(B < 1)
18	9.80	0.5	10.23	0.279	(B < 1)	38	4.967	0.995	9.98	0.097	0.089
19	10.00	1.93	10.0	0.296	0.299	"	4.967	1.990	9.95	0.159	0.150
20	10.00	2.9	9.81	0.395	0.382	"	4.967	3.98	9.84	0.271	0.269
21	10.00	10.0	0.88	0.011	0.010	"	4.967	9.95	9.71	0.630	0.618
22	10.00	10.0	0.37	0.0047	0.0016	39	9.935	0.995	9.98	0.198	179
23	10.00	10.0	1.81	0.0233	0.0388	"	9.935	1.990	9.95	0.290	0.301
24	10.00	10.0	2.85	0.119	0.094	"	9.935	4.975	9.86	0.610	0.562
25	10.00	18.0	0.77	0.013	0.013	40	4.967	0.995	4.98	0.023	0.011
26	20.00	10.0	0.88	0.012	0.023	"	4.967	1.990	4.95	0.031	0.026
27	1.00	0.965	10.10	0.0229	0.018	"	4.967	4.975	4.86	0.055	0.070
28	1.00	1.93	9.95	0.0298	0.0295	"	4.967	9.95	4.71	0.105	0.135

In the experiments of Series E, where the quantity of acid present was small,¹ the rate is much less affected by changes in the concentration of that reagent than the formula requires. Taken alone, this fact might seem to lend plausibility to the view that the action of the hydrogen-ion is catalytic merely, i. e. that the acceleration, not the rate, is proportional to the square of its concentration.² As, however, in the experiments of the same series the rate is only slightly increased by doubling the concentration of the potassium chlorate, it seems preferable to ascribe the deviation to the large excess of neutral salt in the reacting mixture.³

The increased effect of the acid when more than twice normal (Expt. 37) may be due to the occurrence of new reactions — iodates are formed from chlorates and iodides in the presence of strong acid; — and the minimum referred to on page 109 may be compared with the retardation exerted by potassium iodide on the oxidation of sodium thiosulphate, studied by Bell;⁴ experiments with potassium chlorate, potassium iodide, and sulphuric acid might throw light on this subject.

Appendix—H. Schlundt's measurements

In order to compare the results of Schlundt's measurements with those of my own, I have taken advantage of the fact that k_2 is numerically much smaller than k_1 to replace Eq. I by the following simpler form :

$$dx/x\theta = K(A-x)(C-x)^2(B-x) \dots \dots \text{Eq. II.}$$

It is true that on account of the difference between the temperatures at which the two series of experiments were carried out the ratio k_1/k_2 may not be the same in both; but in view of the similarity of the two (hypothetical) reactions involved, and of

¹ Similarly in Expt. 17, 33, and 40, where the quantity of salts is large in comparison with that of the acid, there is a marked discrepancy between R_{obs} and R_{calc} (Table 41).

² Zeit. phys. Chem. 19, 599 (1896).

³ In one case 30 mols of salt to one of acid.

⁴ Jour. Phys. Chem. 7, 79 (1903).

the equality of the temperature coefficients of the rates of most reactions, it is probable that the ratio will not be much affected by the change from 30° to 100° C.

The replacement of $B-1$ by B is, no doubt, responsible for the fall in K when the concentration of the potassium iodide is increased (see below); a term of the form $B-n$, where n was some small number would have given better constants; but without experiments on the position of the minimum rate under the condition of Schlundt's measurements, any value selected for n would have been purely arbitrary.

By means of the integrated forms of Eq. II. a value of K has been computed from each of Schlundt's measurements; the results are contained in Table 42.¹ With the exception of a few scattered instances, obviously due to errors in the experiments, the lowest of the 153 values is 0.98 and the highest 2.5. In view of the fact that in Schlundt's experiments the ratio between the quantities of acid and salt never reached 3 mols of the former to one of the latter, and that in my own work " R_{calc} " differed materially from " R_{obs} " when the ratio fell below 5, the constancy of K is at least as good as could have been expected.

Many of the variations, moreover, can be accounted for — qualitatively at least — without introducing new hypotheses. The fall of K when A is increased, for instance (Table 42, 1a, 1b, 1c), which shows that the rate is not quite proportional to the concentration of the potassium chlorate, is in accordance with those of my own experiments in which small quantities of acid were used; it may be ascribed to the influence of the large amount of salt present, either directly or by modifying the concentrations of the H^+ and ClO_3^- . Similarly with the increase of K when C is decreased (3a, 3c, 3d; 2d, 4c).

¹ The numbers of the experiments (1a, 1b, etc.) are those used by Schlundt; 2a, 3a, and 5a were the same as 1a. The three figures following (for instance, 1.1.1) express the initial concentrations of the chlorate, iodide, and acid in the units defined on page 97. Under "Pct." is given the amount of iodine liberated as a percent of the total possible (in 1a, for instance, "Pct" = 100.1, while in 5c, "pct" = 25.1), and under 10³ K are entered the values of K calculated by Eq. II. and multiplied by 1000.

TABLE XLII.

TABLE XLII.

1a. 1, 1, 1.		1c. 3, 1, 1.		2c. 1, 3, 1.		3c. 1, 1, 3.		4c. 1, 4, 4.	
Pct.	10 ³ K	Pct.	10 ³ K	Pct.	10 ³ K	Pct.	10 ³ K	Pct.	10 ³ K
3.6	2.5	7.0	1.76	4.5	1.62	11.5	1.50	27.0	1.10
7.8	2.6	12.5	1.72	8.1	1.56	22.6	1.76	47.0	1.24
7.5	2.5	20.7	1.63	14.8	1.65	36.9	1.88	61.0	1.27
10.8	2.26	27.4	1.85	20.6	1.56	46.4	1.70	68.5	1.26
11.5	2.1	31.8	1.81	27.6	1.60	59.0	2.12	76.5	1.37
15.0	2.3	41.6	1.72	36.5	1.74	63.4	2.02	82.5	1.42
16.5	2.16	53.6	1.74	44.4	1.83	75.3	2.32	86.5	1.46
17.35	1.7	72.4	1.90	54.3	1.92	87.4	3.37	4d. 1, 2, 6.	
23.5	1.96			60.0	2.17				
30.1	2.13			63.4	2.31				
30.6	2.2	1d. 4, 1, 1.				3d. 1, 1, 4.		36.5	1.5
33.9	2.26							58.0	1.7
36.4	2.2							77.0	1.63
38.9	2.16	7.0	2.88			38.3	1.5	77.3	1.65
40.0	2.06	12.5	1.91	2d. 1, 4, 1.		61.4	2.46	88.5	1.59
42.5	1.9	20.6	1.92			79.3	3.3	90.5	1.15
46.0	2.1	26.5	1.84			92.9	6.4	5b. 2, 2, 2.	
53.3	2.3	33.8	1.90	4.8	1.34	4a. 1, 2, 2.		11.1	1.76
54.3	2.2	38.5	1.90	11.5	1.40			16.6	1.53
58.0	2.3	43.4	1.90	16.8	1.44			29.9	1.60
60.3	2.5	48.1	1.98	23.8	1.56			43.3	1.63
		50.6	2.01	28.8	1.50			50.3	1.56
		53.5	2.10	34.4	1.52	9.4	1.33	56.3	1.53
		60.5	1.70	42.8	1.80	28.4	1.58	59.8	1.46
		64.0	1.70	43.8	1.61	41.3	1.63	62.9	1.46
		68.5	1.57	52.9	1.75	53.3	1.63	66.6	1.40
		69.5	1.56	56.5	1.75	64.4	1.53	73.0	1.50
		78.3	2.20	60.5	1.70	76.0	1.58	76.0	1.50
						84.0	1.88		
1b. 2, 1, 1.		2b. 1, 2, 1.				4b. 1, 3, 3.		5c. 4, 4, 4.	
3.4	1.81								
7.1	2.0	6.0	2.23	3b. 1, 1, 2.				30.3	1.03
9.9	1.99	11.8	2.46			13.0	1.60	42.1	1.06
16.5	1.65	15.9	2.16	10.8	1.90	25.3	1.24	48.0	1.06
16.8	1.94	24.1	2.32	18.1	2.03	43.8	1.50	54.0	0.96
24.8	2.05	28.6	2.38	26.1	2.06	60.0	1.42	63.0	0.96
32.3	1.95	34.6	2.33	31.8	2.02	70.8	1.49	69.5	1.00
42.3	2.13	41.8	2.38	40.5	2.06	81.3	1.64	73.4	0.96
27.4	1.85	46.4	2.33	47.4	2.07	89.3	1.80	77.2	1.06
53.0	1.70	49.8	2.10	57.5	2.36	99.0	2.8	81.25	1.16
64.6	1.60	63.4	3.5						

The increase of K with x observable in many of the experiments (2c, 2d, 3b, 3c, 3d, 4b, 4c) is just what would happen if K were calculated by Eq. II. from the data afforded by a reaction which in reality proceeded according to Eq. I.; the same can be said of the decrease of K when B is increased (2a, 2b, 2c, 2d; 3d, 4c; 3b, 4a). Finally the retardation caused by free iodine accumulated in the solution shows itself in some cases by a regular diminution of K from the beginning of the experiment until iodine was precipitated; one would expect this effect to be most marked when the concentration of the potassium iodide was low (cf. 2a with 2d).

Temperature coefficient

If $B = C$, then K of Eq. II calculated from the initial rate ($x = 0$) is equal to $k_1 + k_2$. For Expt. 5 then, $K = 0.00000146$ at 30°C . The experiment of Schlundt's where the ratios between the initial concentrations are most like those of Expt. 5, is Expt. 4c with $K(x = 0) = 0.0011$ at 100°C . Adopting the usual logarithmic formula, this corresponds to doubling the rate every 8.6 degrees.

In conclusion, I wish to express my thanks to Prof. W. Lash Miller, at whose suggestion this research was undertaken, and under whose direction it has been carried out.

*University of Toronto,
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